(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 749 155 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
18.12.1996 Bulletin 1996/51

(51) Int Cl.[6] **H01L 21/314**, H01L 23/29, C04B 41/50

(21) Application number: **96304287.4**

(22) Date of filing: **07.06.1996**

(84) Designated Contracting States:
DE FR GB IT NL

(30) Priority: **16.06.1995 US 491071**

(71) Applicant: **DOW CORNING CORPORATION**
Midland, Michigan 48686-0994 (US)

(72) Inventors:
- **Haluska, Loren Andrew**
  Midland, Michigan 48640 (US)
- **Michael, Keith Winton**
  Midland, Michigan 48640 (US)

(74) Representative: **Lewin, John Harvey**
Elkington and Fife,
Prospect House,
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)

(54) Composite electronic coatings

(57) The present invention provides a method of forming composite coatings on electronic substrates and the substrates coated thereby. The method comprises applying a coating comprising a polysilazane and a refractory fiber on an electronic substrate and then heating the coated substrate at a temperature sufficient to convert the polysilazane into a ceramic.

EP 0 749 155 A2

Printed by Jouve, 75001 PARIS (FR)

lenc™. Al_2O_3-ZrO_2 fibers with a diameter of 20 micrometers manufactured by Du Pont™ and designated "PRD-166" carbon fibers such as those sold by Hitco™ and aramide fibers sold under the tradename "KEVLAR"™ by DuPont™.

The refractory fibers used herein are chopped into short lengths for ease in coating. Any fiber length which can be manipulated into the desired coating is used herein. Generally, the lengths are less than 1 centimeter with lengths in the range of between 10 micrometers to 10 millimeters being preferred.

The amount of refractory fibers used in the present invention can also be varied over a wide range depending, for example, on the characteristics desired in the final coating. Generally, however, the refractory fibers are used in an amount less than 90 volume percent to insure that enough resin is present to bind the refractory fibers. Obviously, smaller amounts of fibers (e.g., 1-5 vol%) can also be used. Preferred are fiber volumes in the range of between 25 and 80%.

If desired, other materials may also be present in the coating composition. For instance, it is within the scope of the present invention to use a material which modifies the surface of the fiber for better adhesion or for better release. Typically, such agents are included in amounts from 0.1 to 5 wt%. Such materials can include, for example, silanes such as glycidoxypropyltrimethoxysilane, mercaptopropyltrimethoxysilane and vinyltriacetoxysilane. Similarly, it is within the scope of the invention to include suspending agents in the coating composition. These and other optional components are known to those skilled in the art.

According to our invention, the polysilazane, refractory fibers and any optional components are applied to the surface of an electronic substrate. The surface of the electronic substrate can be bare (i.e., no passivation) or the circuit can have a passivation. Such passivation can be, for example, ceramic coatings such as silica, silicon nitride, silicon carbide, silicon oxynitride and silicon oxycarbide, deposited by, for example, CVD, PVD or sol-gel procedures. Such passivation is known to those skilled in the art. Likewise, the circuit can be pre or post interconnected.

The coating composition can be applied in any manner, but a preferred method involves dissolving the polysilazane in a solvent and then dispersing the fiber and any optional components therein. This dispersion is next applied to the surface of an electronic substrate. Various facilitating measures such as stirring and/or heating may also be used to dissolve or disperse the polysilazane and fiber and to create a more uniform application material. Solvents which may be used include any agent or mixture of agents that will dissolve the polysilazane and disperse the fiber to form a uniform liquid mixture without affecting the resultant coating. These solvents can include, for example, aromatic hydrocarbons such as benzene or toluene, alkanes such as n-heptane or dodecane; ketones, alcohols; esters; ethers, and cyclic dimethylpolysiloxanes in an amount sufficient to dissolve/disperse the above materials to the concentration desired for application. Generally, the solvent is used to form a 0.1-80 weight percent mixture, preferably 1-50 wt%.

If a liquid method is used, the liquid mixture comprising the polysilazane, refractory fiber, solvent and any optional components is then coated onto the substrate. The method of coating can be, but is not limited to, spin coating, dip coating, spray coating or flow coating. Other equivalent means, however, are also deemed to be within the scope of this invention.

The solvent is then allowed to evaporate from the coated substrate resulting in the deposition of the polysilazane and refractory fiber coating. Any suitable means of evaporation may be used such as simple air drying by exposure to an ambient environment, by the application of a vacuum or mild heat (e.g., less than 50°C.) or during the early stages of the heat treatment. It is noted that when spin coating is used, the additional drying period is minimized as the spinning drives off the solvent.

Although the above methods primarily focus on using a liquid approach, one skilled in the art would recognize that other equivalent means such as melt deposition would also function herein.

The polysilazane is then typically converted to the ceramic by heating it to a sufficient temperature. Generally, the temperature is in the range of 50 to 1000°C. depending on the pyrolysis atmosphere. Preferred temperatures are in the range of 50 to 800°C., and more preferably 50-500°C. Heating is generally conducted for a time sufficient to ceramify, generally up to 6 hours, with less than 3 hours being preferred.

The above heating may be conducted at any effective atmospheric pressure from vacuum to superatmospheric and under any effective oxidizing or non-oxidizing gaseous environment such as air, O_2, an inert gas (N_2, Ar, etc.), ammonia, amines, moisture, N_2O and hydrogen.

Any method of heating such as the use of a convection oven, rapid thermal processing, hot plate or radiant or microwave energy is generally functional herein. The rate of heating, moreover, is also not critical, but it is most practical and preferred to heat as rapidly as possible.

By the above methods, a ceramic coating is produced on the substrate. The thickness of the coating can vary over a wide range (e.g., up to 500 micrometers). These coatings smooth the irregular surfaces of various substrates (i.e., planarizing), they are relatively defect free, they have excellent adhesive properties; they provide mechanical and electrical protection and they are opaque. Moreover, the fibers provide added strength and toughness to our coatings.

Additional coatings may be applied over these coatings if desired. These include, for example, SiO_2 coatings, SiO_2/ceramic oxide layers, silicon containing coat-

ings silicon carbon containing coatings silicon nitrogen containing coatings, silicon oxygen nitrogen coatings silicon nitrogen carbon containing coatings, organic coatings, silicone coatings and/or diamond like carbon coatings. Methods for the application of such coatings are known in the art and many are described in US-A 4,756,977. An especially preferred coating is silicon carbide applied by the chemical vapor deposition of silacyclobutane or trimethylsilane. This process is further described in US-A 5,011,706.

The following non-limiting examples are included so that one skilled in the art may more readily understand the invention.

Example 1

Hydridopolysilazane resin, 2 g, produced by the method of US-A 4,540,803, 1 g of silicon carbide whiskers from Tateho Chemical Industries Co. Ltd. (0.5 x 15-20 micrometers), 0.4 g of glycidoxypropyltrimethoxysilane and 2.5 g of cyclic polydimethylsiloxanes were mixed with a sonic probe to form a coating solution. An 11.25 cm^2 alumina panel was coated with the solution by using a 75 micrometer drawdown bar. The coated panel was air dried for 3 hours and then pyrolyzed for 2 hours at 400°C. in air. The pyrolyzed coating was examined with a microscope and found to have no cracks at 1000x magnification. The coating thickness was 22.3 micrometers.

Example 2

Borohydridopolysilazane resin, 2 g, produced by the method of US-A 5,169,908, 1 g of the above silicon carbide whiskers, 0.4 g of glycidoxypropyltrimethoxysilane and 2.0 g of cyclic polydimethylsiloxanes were mixed with a sonic probe to form a coating solution. A similar alumina panel was coated with the solution by using the same drawdown bar. The coated panel was air dried for 3.5 hours and pyrolyzed for 1 hour at 400°C. in air. The pyrolyzed coating was examined with a microscope and also found to have no cracks at 1000x magnification. The coating thickness was 18.2 micrometers.

Claims

1. A method of forming a composite coating on an electronic substrate comprising applying a coating composition comprising a polysilazane and refractory fibers onto the electronic substrate and heating the coated electronic substrate at a temperature sufficient to convert the polysilazane into a ceramic.

2. The method of claim 1 wherein the refractory fiber is selected from the group consisting of carbon, silicon carbide, silicon nitride, aluminum oxide, organic fiber and aramide fiber.

3. The method of claim 1 or 2 wherein the coated substrate is heated at a temperature in the range of between 50°C. and 1000°C. for less than 6 hours.

4. The method of any of claims 1 to 3 wherein the coating composition also contains a material which modifies the surface of the refractory fiber for better adhesion of the ceramic.

5. The method of any of claims 1 to 4 wherein the coating composition also contains an amount of an agent effective to improve the suspension of the fiber in the coating composition.

6. The method of any of claims 1 to 5 wherein the fiber is present in the coating composition in an amount less than 90 volume percent.

7. The method of any of claims 1 to 6 wherein the polysilazane is selected from the group consisting of hydridopolysilazane, methylpolydisilylazane and polyborosilazane.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 749 155 A3

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
14.05.1997 Bulletin 1997/20

(43) Date of publication A2:
18.12.1996 Bulletin 1996/51

(21) Application number: **96304287.4**

(22) Date of filing: **07.06.1996**

(51) Int Cl 6 **H01L 21/316**, C04B 35/622, C04B 41/87, H01L 23/29, H01L 21/56

(84) Designated Contracting States:
DE FR GB IT NL

(30) Priority: **16.06.1995 US 491071**

(71) Applicant: **DOW CORNING CORPORATION**
Midland, Michigan 48686-0994 (US)

(72) Inventors
- **Haluska, Loren Andrew**
  Midland, Michigan 48640 (US)
- **Michael, Keith Winton**
  Midland, Michigan 48640 (US)

(74) Representative: **Lewin, John Harvey**
Elkington and Fife,
Prospect House,
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)

(54) Composite electronic coatings

(57) The present invention provides a method of forming composite coatings on electronic substrates and the substrates coated thereby. The method comprises applying a coating comprising a polysilazane and a refractory fiber on an electronic substrate and then heating the coated substrate at a temperature sufficient to convert the polysilazane into a ceramic.

EP 0 749 155 A3

Printed by Jouve, 75001 PARIS (FR)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 4287

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 549 224 A (DOW CORNING) 30 June 1993 * page 2, line 23 - page 7, line 20; claims 1-21 *	1-7	H01L21/316 C04B35/622 C04B41/87 H01L23/29 H01L21/56
A	EP 0 611 067 A (DOW CORNING) 17 August 1994 * page 2, line 20 - page 4, line 45; claims 1-8; table 1 *	1,3,7	
P,X	EP 0 677 871 A (DOW CORNING) 18 October 1995 * column 1, line 36 - column 4, line 39; claims 1-10 *	1-7	
A	US 5 258 229 A (LUM GENEVIEVE S ET AL) 2 November 1993 * column 1, line 61 - column 2, line 17 * * column 3, line 17 - column 4, line 27 * * claims 1-12 *	1-7	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
H01L
C04B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 March 1997	Königstein, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)